

THE DISTRIBUTION OF DEUTERATED FORMALDEHYDE WITHIN ORION-KL

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ABSTRACT

We report the first high angular resolution imaging ($3''.4 \times 3''.0$) of deuterated formaldehyde (HDCO) toward Orion-KL, carried out with the Submillimeter Array. We find that the spatial distribution of the formaldehyde emission systematically differs from that of methanol: while methanol is found toward the inner part of the region, HDCO is found in colder gas that wraps around the methanol emission on four sides. The HDCO/H₂CO ratios are determined to be 0.003–0.009 within the region, up to an order of magnitude higher than the D/H measured for methanol. These findings strengthen the previously suggested hypothesis that there are differences in the chemical pathways leading to HDCO (via deuterated gas-phase chemistry) and deuterated methanol (through conversion of formaldehyde into methanol on the surface of icy grain mantles).

Key words: astrochemistry – ISM: abundances – ISM: individual objects (Orion-KL) – ISM: molecules – line: identification

1. INTRODUCTION

The Orion-KL nebula, which lies at a distance of 414 ± 7 pc (Menten et al. 2007), is a focal source for studies of the physics and chemistry of high-mass star forming regions. Its rich molecular diversity and complex physical structure have been revealed by a number of spectral line surveys and interferometric studies of the region (e.g., Blake et al. 1987; Schilke et al. 1997, 2001; Beuther et al. 2005, 2006; Comito et al. 2005; Persson et al. 2007; Friedel & Snyder 2008; Guélin et al. 2008; Tercero et al. 2010, 2011; Favre et al. 2011a, 2011b, 2014; Friedel & Widicus Weaver 2012; Widicus Weaver & Friedel 2012; Brouillet et al. 2013; Esplugues et al. 2013; Peng et al. 2013). Recently, a broadband spectral line survey of Orion-KL carried out with the *Herschel*/HIFI spectrometer (Bergin et al. 2010; Crockett et al. 2010, 2014) has been obtained as part of the HEXOS key program.⁶ The unprecedented 1.2 THz wide frequency coverage of this survey has allowed for strong constraints on physical parameters and molecular abundances due to the detection of many transitions for each molecule with a wide range of excitation conditions, revealing the presence of thermal gradients (e.g., Wang et al. 2011). Among the molecular components associated with Orion-KL lie the so-called Hot Core and Compact Ridge. Although the precise nature of these regions remains enigmatic, evidence has been recently provided that they may have originated from the interaction of the remnants of a recent explosion with ice grains mantles (≤ 720 years ago, e.g., Gómez et al. 2005, 2008; Rodríguez et al. 2005; Bally et al. 2011; Nissen et al. 2012), leading to the evaporation and the heating of organic material (Favre et al. 2011a; Zapata et al. 2011).

Deuterium fractionation is intrinsically a low-temperature process. Therefore, deuterated molecules in warm ($T \geq 100$ K) regions, such as Orion-KL, offer a window into its physical conditions at the earlier, colder stage ($T \sim 10$ – 30 K) when this

material likely formed (Blake et al. 1987; Pagani et al. 1992; Charney et al. 1997). Numerous deuterated species have been observed toward Orion-KL: deuterated water (Turner et al. 1975; Jacq et al. 1990; Neill et al. 2013b), deuterated ammonia (Rodríguez Kuiper et al. 1978; Walmsley et al. 1987), deuterated formaldehyde (Loren & Wootten 1985; Turner 1990), and deuterated methanol (Mauersberger et al. 1988; Jacq et al. 1993; Peng et al. 2012). Recently, Neill et al. (2013a) used the HIFI survey and tens of transitions to set strong constraints in the D/H ratio of organics associated with Orion-KL. Their finding strongly suggests that D/H fractionation is inhomogeneous in this source.

In this study, we extend the HIFI study of deuterated species performed by Neill et al. (2013a, 2013b); especially since the *Herschel* observations are spatially unresolved, even with well-determined column densities within the beam, there can be large deviations in the deuterium fractionation as a function of spatial position. In Section 2, we present the Submillimeter Array (SMA) observations to complement the HIFI analysis. In particular, we focus on formaldehyde (H₂CO and HDCO). The D/H ratios of this molecule is key to obtaining a full picture of the oxygen chemistry in this region, as formaldehyde is believed to be an intermediate in the grain-surface synthesis of methanol through sequential reactions of H or D atoms with CO (see Watanabe & Kouchi 2002; Cazaux et al. 2011; Taquet et al. 2012). Alternatively, gas-phase chemistry might independently lead to the formation of formaldehyde via reactions involving CH₂D⁺ products under warmer conditions (typically $T > 50$ K, see Loren & Wootten 1985; Wootten 1987). Incidentally, the tentative detection of the CH₂D⁺ ion toward Orion-KL by Roueff et al. (2013) suggests that gas-phase chemistry might be efficient for the HDCO formation. In this analysis, we present the first high angular resolution image of the spatial distribution of (deuterated) formaldehyde in Orion-KL and discuss the different chemical pathways that can be involved in its formation. More specifically, results and analysis are presented in Section 3 and discussed in Section 4, with conclusions set out in Section 5.

⁶ www.hexos.org

Table 1
Spectroscopic and Observational Line Parameters for Formaldehyde^{a,b}

HDCO															
Frequency (MHz)	Transition	E_{up} (K)	A $\times 10^{-4}$ (s^{-1})	Synthesized		dF1					dF2				
				Beam		$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)	$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)
				($'' \times ''$)	PA ($^{\circ}$)										
192893.26 ^{c, d}	$3_{0,3}-2_{0,2}$	18.5	1.94
193907.46	$3_{2,1}-2_{2,0}$	50.4	1.10	3.44×3.01	30	8.50(1.54)	9.84(0.14)	1.80(0.46)	89(16)	4.65(0.86)	7.38(0.43)	7.75(0.10)	2.20(0.18)	56(7)	2.92(0.22)
193391.61	$3_{2,2}-2_{2,1}$	50.4	1.09	3.47×3.02	30	9.05(0.63)	9.65(0.10)	1.69(0.16)	89(16)	4.96(0.37)	7.07(0.35)	7.57(0.07)	2.40(0.15)	56(7)	2.80(0.18)
						dF3					dF4				
Frequency (MHz)	Transition	E_{up} (K)	A $\times 10^{-4}$ (s^{-1})	Synthesized		$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)	$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)
192893.26 ^{c, d}	$3_{0,3}-2_{0,2}$	18.5	1.94
193907.46	$3_{2,1}-2_{2,0}$	50.4	1.10	3.44×3.01	30	7.13(0.98)	7.80(0.10)	1.71(0.32)	57(8)	2.77(0.42)	11.25(1.45)	8.61(0.05)	1.13(0.14)	52(8)	4.26(0.62)
193391.61	$3_{2,2}-2_{2,1}$	50.4	1.09	3.47×3.02	30	8.00(2.29)	8.00(0.03)	1.39(0.44)	57(8)	3.12(0.93)	9.79(1.02)	8.30(0.10)	1.66(0.24)	52(8)	3.71(0.45)
(para-)H $_2^{13}$ CO															
Frequency (MHz)	Transition	E_{up} (K)	A $\times 10^{-4}$ (s^{-1})	Synthesized		dF1					dF2				
				beam		$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)	$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)
				($'' \times ''$)	PA ($^{\circ}$)										
212811.18	$3_{0,3}-2_{0,2}$	20.4	2.64	3.17×2.75	30	17.99(1.73)	9.88(0.09)	1.83(0.24)	89(16)	5.44(0.53)	16.04(1.37)	7.44(0.11)	2.54(0.29)	56(7)	2.83(0.26)
213037.34 ^d	$3_{2,2}-2_{2,1}$	67.7	1.46
213293.57	$3_{2,1}-2_{2,0}$	67.7	1.46	3.15×2.75	30	5.87(0.85)	9.89(0.19)	2.21(0.42)	89(16)	5.43(0.82)	3.84(0.40)	7.43(0.13)	2.16(0.30)	56(7)	2.83(0.35)
						dF3					dF4				
Frequency (MHz)	Transition	E_{up} (K)	A $\times 10^{-4}$ (s^{-1})	Synthesized		$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)	$\int T_{\text{mb}} dv$ (K km s $^{-1}$)	v_{LSR} (km s $^{-1}$)	Δv_{LSR} (km s $^{-1}$)	T_{ex} (K)	N (10^{14} cm $^{-2}$)
212811.18	$3_{0,3}-2_{0,2}$	20.4	2.64	3.17×2.75	30	12.93(0.28)	7.94(0.03)	1.55(0.04)	57(8)	2.27(0.64)	9.70(1.16)	8.44(0.03)	1.58(0.25)	52(8)	1.58(0.20)
213037.34 ^d	$3_{2,2}-2_{2,1}$	67.7	1.46
213293.57	$3_{2,1}-2_{2,0}$	67.7	1.46	3.15×2.75	30	3.14(0.55)	8.03(0.08)	1.56(0.37)	57(8)	2.27(0.44)	2.16(0.26)	8.63(0.17)	1.30(0.23)	52(8)	1.58(0.23)

Notes. The HDCO emission peaks lie at the following positions: dF1 ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}601$, $\delta_{J2000} = -05^{\circ}22'34''.18$), dF2 ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}054$, $\delta_{J2000} = -05^{\circ}22'27''.82$), dF3 ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}210$, $\delta_{J2000} = -05^{\circ}22'42''.88$), and dF4 ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}13^{\text{s}}861$, $\delta_{J2000} = -05^{\circ}22'41''.92$). The excitation temperature of HDCO toward those peaks is fixed and taken equal to that of H $_2^{13}$ CO as described in Section 3.2.

^a Measured and predicted transitions are available from the CDMS (<http://www.astro.uni-koeln.de/cdms/>; Müller et al. 2005) database and at Splatalogue (www.splatalogue.net; Remijan et al. 2007). More specifically and as previously reported by Neill et al. (2013a), we used the spectroscopic data parameters from Müller et al. (2000) for H $_2^{13}$ CO and from Bocquet et al. (1999) and Johns & McKellar (1977) for HDCO.

^b The numbers in brackets refer to the 1σ level uncertainty.

^{c,d} These two lines have been excluded from our analysis since their emission is contaminated by the emission from HCOOCH $_3$ and ^{33}SO , respectively.

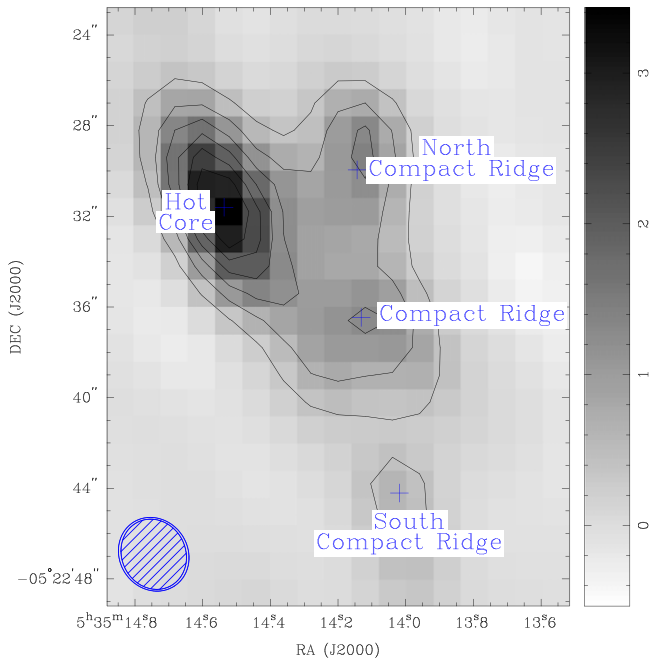


Figure 1. Continuum emission maps obtained at 213 GHz (grayscale, USB band) and at 198 GHz (black, LSB band) toward Orion-KL as measured with the SMA. The first contour and the level step are at 3σ (where $1\sigma = 0.132 \text{ Jy beam}^{-1}$). The synthesized beams are $3''.2 \times 2''.8$ (P.A. = $26^\circ.7$) and $3''.5 \times 3''.01$ (P.A. = $32^\circ.7$) at 207 and 198 GHz, respectively. Blue crosses mark the positions of the four main continuum sources derived from Gaussian fits in the (u, v) plane (198 GHz data set, LSB band). These sources are the Hot core ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}537$, $\delta_{J2000} = -05^\circ22'31''.600$), the Compact Ridge ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}132$, $\delta_{J2000} = -05^\circ22'36''.462$), the North Compact Ridge ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}144$, $\delta_{J2000} = -05^\circ22'29''.295$), and the South Compact Ridge ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}019$, $\delta_{J2000} = -05^\circ22'44''.212$).

2. OBSERVATIONS AND DATA REDUCTION

Observations of Orion-KL were carried out with the SMA⁷ (Ho et al. 2004) in its compact configuration on 2013 December 12 for about 6.75 hr. The phase-tracking center was $\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}.20$, $\delta_{J2000} = -05^\circ22'33''.00$. The new broader-bandwidth SMA capability of the 230 GHz band was used to cover the following frequency ranges: 192.6–194.6 GHz and 197.6–199.6 GHz in LSB band, and 207.6–209.6 GHz and 212.6–214.6 GHz in the USB band. An enormous advantage of this broadband capability is the possibility to observe transitions of both HDCO and H_2^{13}CO in a single tuning (see Table 1). The correlator was configured with a uniform spectral resolution over 4 GHz bandwidth in each sideband. Each 4 GHz bandwidth is divided into 48 “chunks” and each chunk is further divided into 128 channels with a channel width of 0.812 MHz. The weather conditions were good and stable with an atmospheric opacity of about 0.14 at 225 GHz. The SMA data were calibrated using the MIR/IDL package⁸ (Qi 2007). The nearby quasars 0423–013 and 0510+180 were used as complex gain (phase and amplitude) calibrators.

Continuum subtraction and data imaging were performed using the MIRIAD software package. The final continuum emission maps obtained at 198 and 213 GHz are shown in

Figure 1. They were restored using a robust weighting of 0.0, resulting in a synthesized beam size of $3''.5 \times 3''.01$ (P.A. = $32^\circ.7$) at 198 GHz and of $3''.2 \times 2''.8$ (P.A. = $26^\circ.7$) at 213 GHz. Positions of the four main continuum sources derived from Gaussian fits in the (u, v) LSB data set image plane are given in Figure 1. The positions of these continuum sources are commensurate between the LSB and USB data sets and, in agreement, within the synthesized beam size, with previous PdBI observations (Favre et al. 2011a).

In this analysis, we only focus on two emission lines of HDCO and two of para- H_2^{13}CO (see spectroscopic parameters listed in Table 1). The spectral resolution is 1.14 km s^{-1} for H_2^{13}CO at 212/213 GHz and 1.26 km s^{-1} for the HDCO lines at 193 GHz. The resulting synthesized beam sizes ($\sim 3'' \times 3''$, P.A. = 30°) are given in Table 1 at the different frequencies.

3. RESULTS AND ANALYSIS

3.1. Emission Maps and Velocity Structure

The HDCO and H_2^{13}CO emission maps integrated over the line profile are shown in Figure 2. Four main molecular emission peaks, labeled dF1 to dF4, are associated with the HDCO emission. More specifically, they are located toward the left of the Hot Core component (dF1), north of the Compact Ridge (dF2), and in the quiescent ridge (dF3 and dF4) located south of the Compact Ridge. Their coordinates are given in Table 1. The regions dF1, dF2, and dF3 are also associated with the H_2^{13}CO emission, but dF4 is not. Incidentally, it is important to note that the integrated emission map of the H_2^{13}CO transition at 213293.57 MHz is strongly contaminated by the emission from an unidentified species toward the Hot Core region. This is shown in Figure 3, which displays the integrated emission map along with the spectrum of this H_2^{13}CO line; the latter being taken at the position of the contaminated emission peak.

The spectra of the formaldehyde transitions observed toward regions dF1 to dF4 are shown in Figure 4 and the observed line parameters are summarized in Table 1. The bulk of the formaldehyde emission toward those peaks appears to lie between $v_{\text{LSR}} = 7.5 \text{ km s}^{-1}$ and $v_{\text{LSR}} = 9.8 \text{ km s}^{-1}$. This result is consistent with the HDCO LSR velocity derived by Loren & Wootten (1985) toward the quiescent ridge ($\sim 8.5 \text{ km s}^{-1}$, single-dish Millimeter Wave Observatory observations) and by Neill et al. (2013a) toward the region (~ 8 and 10.4 km s^{-1} , *Herschel*/HIFI observations). It is important to note that Neill et al. (2013a) associated the HDCO emission with two velocity components in the Compact Ridge. This difference results from the fact that (i) some complex molecules, such as methyl formate or dimethyl ether, are seen with two distinct velocity components emitting at ~ 7.5 and 9.2 km s^{-1} in the Compact Ridge (e.g., Favre et al. 2011a; Brouillet et al. 2013), and that (ii) the *Herschel* observations are spatially unresolved. We infer that the two HDCO velocity components seen by Neill et al. (2013a) actually correspond to our HDCO emission observed toward dF3 and dF1, respectively.

3.2. Excitation Temperature

Assuming optically thin emission, we use the integrated line intensity measurements of the observed H_2^{13}CO transitions to derive the formaldehyde excitation temperature (T_{ex}) within

⁷ The SMA is a joint project between the Smithsonian Astrophysical Observatory and the Academia Sinica Institute of Astronomy and Astrophysics, and is funded by the Smithsonian Institution and the Academia Sinica.

⁸ <https://www.cfa.harvard.edu/~cqi/mircook.html>

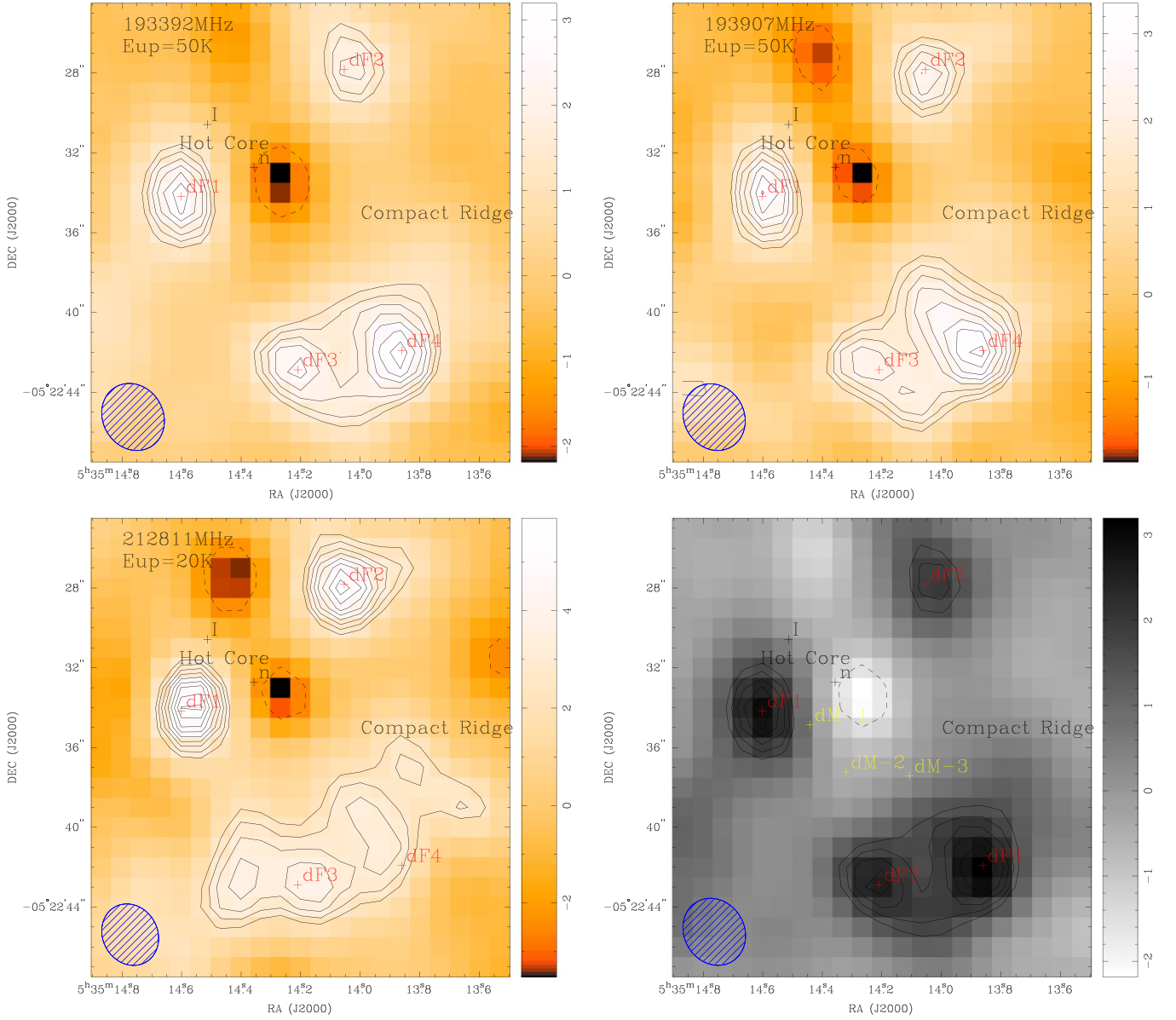


Figure 2. Formaldehyde integrated emission maps from $v_{\text{LSR}} = 6.5 \text{ km s}^{-1}$ to $v_{\text{LSR}} = 10.0 \text{ km s}^{-1}$. Red crosses indicate the position of the regions dF1 to dF4. Black crosses indicate the positions of the radio source I ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}.5141$, $\delta_{J2000} = -05^{\circ}22'30''.575$) and the IR source n ($\alpha_{J2000} = 05^{\text{h}}35^{\text{m}}14^{\text{s}}.3571$, $\delta_{J2000} = -05^{\circ}22'32''.719$; Goddi et al. 2011b). Top: HDCO emission at 193391.6 MHz (left panel) and 193907.5 MHz (right panel). Bottom left: H_2^{13}CO emission at 212811.2 MHz. The first contour is at 5σ and the level step at 1σ (where $\sigma = 0.27$ and $0.44 \text{ Jy beam}^{-1} \text{ km s}^{-1}$ for HDCO and H_2^{13}CO , respectively). Bottom right: same as the top left panel, expect for the indicated deuterated methanol emission peaks (in yellow) identified by Peng et al. (2012).

Orion-KL following Equation (1):

$$T_{\text{ex}} = -\frac{h\nu}{k_B \ln \left(\frac{g_l A_l \nu_u^2 W_u}{g_u A_u \nu_l^2 W_l} \right)} = -\frac{E_u - E_l}{\ln \left(\frac{g_l A_l \nu_u^2 W_u}{g_u A_u \nu_l^2 W_l} \right)}, \quad (1)$$

where E , W , A , g , and ν refer to the state energies (K), the integrated line intensities (K km s^{-1}), the Einstein A coefficients (s^{-1}), the statistical weights, and the line frequencies (Hz) of the $3_{2,1}-2_{2,0}$ (u) and $3_{0,3}-2_{0,2}$ (l) transitions. It is important to note that Equation (1) cannot be directly applied to HDCO since both of the detected transitions have the same upper energy level (see Table 1). Thus, the below analysis

hinges on the assumption that T_{ex} is the same for both HDCO and H_2^{13}CO .

Figure 5(a) presents the excitation temperature map for H_2^{13}CO within Orion-KL. The formaldehyde excitation temperature derived toward the dF2, dF3, and dF4 peaks is low (52–57 K, see Table 1), contrary to dF1 for which it is higher (~ 90 K). Our derived temperatures in the quiescent ridge (i.e., regions dF3 and dF4) are commensurate within the uncertainties with that derived by Bergin et al. (1994, 60 ± 30 K) using $\text{CH}_3\text{C}_2\text{H}$, a known tracer of ambient ridge gas. Regarding the dF2 emission peak, our derived temperature is in agreement with a KL–W methanol clump that lies in its vicinity (i.e., $\sim 2''$ east, see Peng et al. 2012). As for the dF1 emission peak, there is a slight discrepancy with the temperature derived by Peng et al. (2012). In particular, these

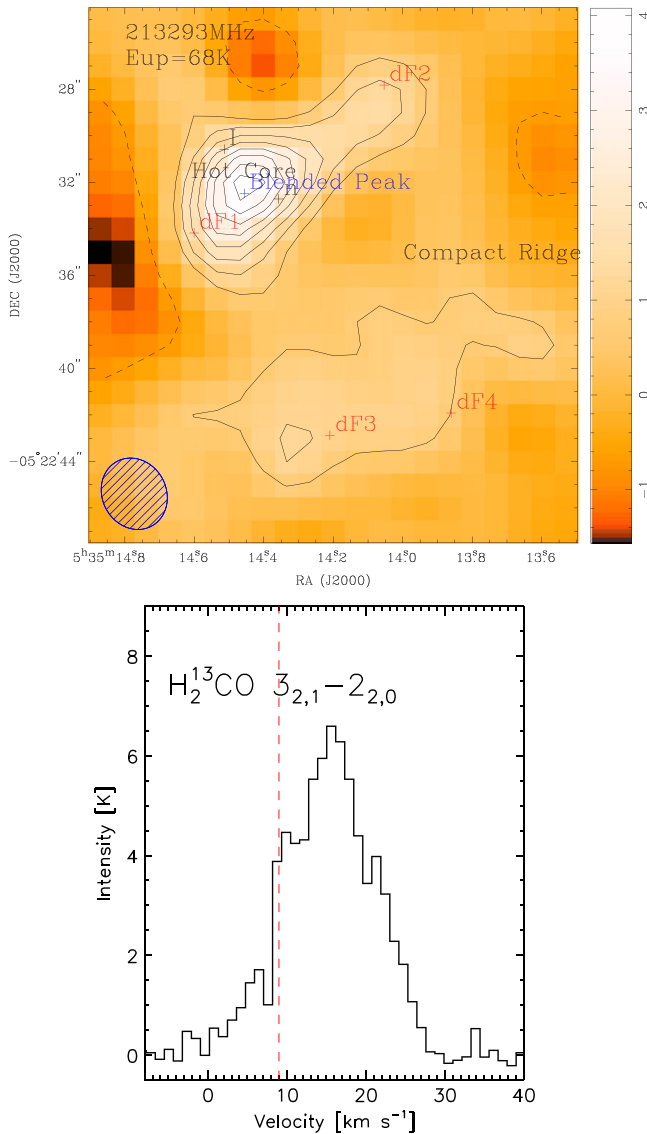


Figure 3. Top: H_2^{13}CO integrated emission map at 213293.6 MHz from $v_{\text{LSR}} = 6.5 \text{ km s}^{-1}$ to $v_{\text{LSR}} = 10.0 \text{ km s}^{-1}$. Red crosses indicate the position of the regions dF1 to dF4 while black crosses indicate the positions of the radio source I and the IR source n (see Figure 2). The first contour is at 3σ and the level step is at 2σ (where $\sigma = 0.27 \text{ Jy beam}^{-1} \text{ km s}^{-1}$). The emission of this H_2^{13}CO transition is strongly contaminated by the emission from an unidentified species toward the Hot Core region marked by a blue cross and labeled “Blended Peak.” Bottom: H_2^{13}CO spectrum observed toward the “Blended Peak” position (blue cross). The red dashed line indicates an LSR velocity of 9.0 km s^{-1} .

authors report a temperature that is lower than the typical temperature derived in the vicinity of this region ($\sim 100\text{--}300 \text{ K}$, e.g., Friedel & Snyder 2008; Favre et al. 2011a; Goddi et al. 2011a). However, looking at their Figure B.4., a 130 K temperature seems to be consistent with their data, suggesting that their error bars might have been underestimated. Overall the temperatures derived here are lower than the typical temperatures derived for organic species toward the Hot Core and Compact Ridge components associated with the inner part of Orion-KL (e.g., Crockett et al. 2014).

3.3. Column Density

Assuming that (i) LTE is reached, which implies that the excitation temperature is equal to the rotational temperature,

and (ii) the rotational temperature is the same for both HDCO and H_2^{13}CO , we derive the total column density, N , by using the following equation (Goldsmith & Langer 1999):

$$\ln \left(\frac{8\pi k_B \nu^2 W}{g_u h c^3 A_{ul}} \right) = \ln \left(\frac{N}{Q} \right) - \frac{E_u}{T}, \quad (2)$$

where

W	is the integrated line intensity (K cm s^{-1}),
ν	is the line frequency (Hz),
A_{ul}	is the Einstein coefficient (s^{-1}),
g_u	is the statistical weight,
N	is the total column density (cm^{-2}),
Q	is the partition function,
E_{up}	is the upper state energy (K),
h	is the Planck constant (erg s),
k_B	is the Boltzmann constant (erg K^{-1}),
c	is the speed of light (cm s^{-1}), and
T	is the excitation temperature derived above (in K, Section 3.2).

The column densities derived toward regions dF1 to dF4 for both HDCO and para- H_2^{13}CO are listed in Table 1. In addition, Table 2 gives the total column densities for HDCO, H_2^{13}CO , and H_2CO toward the dF1 to dF4 peaks. The total column densities have been calculated as follow: (i) the column densities derived for the two HDCO transitions, which are listed in Table 1, have been averaged. The same applies to the two para- H_2^{13}CO transitions. (ii) Regarding H_2^{13}CO and HDCO, we assume an ortho:para ratio of 3:1, which is commensurate with measurements performed toward Orion-KL by Kahane et al. (1984) and Crockett et al. (2014), and a $^{12}\text{C}/^{13}\text{C}$ isotopic ratio of 70 (see Favre et al. 2014 and reference therein), which is in agreement within the error bars with previous studies (e.g., Persson et al. 2007; Stahl et al. 2008).

3.4. D/H Ratios for Formaldehyde

Using the total column densities for HDCO and H_2^{13}CO (see Section 3.3 and Table 2), we derive the D/H ratio for regions dF1 to dF4. The resulting D/H ratios are given in Table 2. Figure 5(b) shows the distribution map of the D/H ratio for formaldehyde in Orion-KL. The HDCO/ H_2CO ratio is found to be 0.009 ± 0.002 toward dF4, 0.003 ± 0.001 toward dF1, and 0.004 ± 0.001 and 0.005 ± 0.002 toward dF2 and dF3, respectively. Our results are commensurate within the uncertainties from previous D/H ratio measurements in the region (e.g., Loren & Wootten 1985; Neill et al. 2013a) and suggest a possible gradient in the HDCO/ H_2^{13}CO ratio at the 3σ level.

4. DISCUSSION

4.1. Anticorrelation between Formaldehyde and Methanol Emission

A recent study by Peng et al. (2012) using the Plateau de Bure interferometer derived the D/H ratios of methanol (CH_2DOH and CH_3OD) at comparable resolution to our

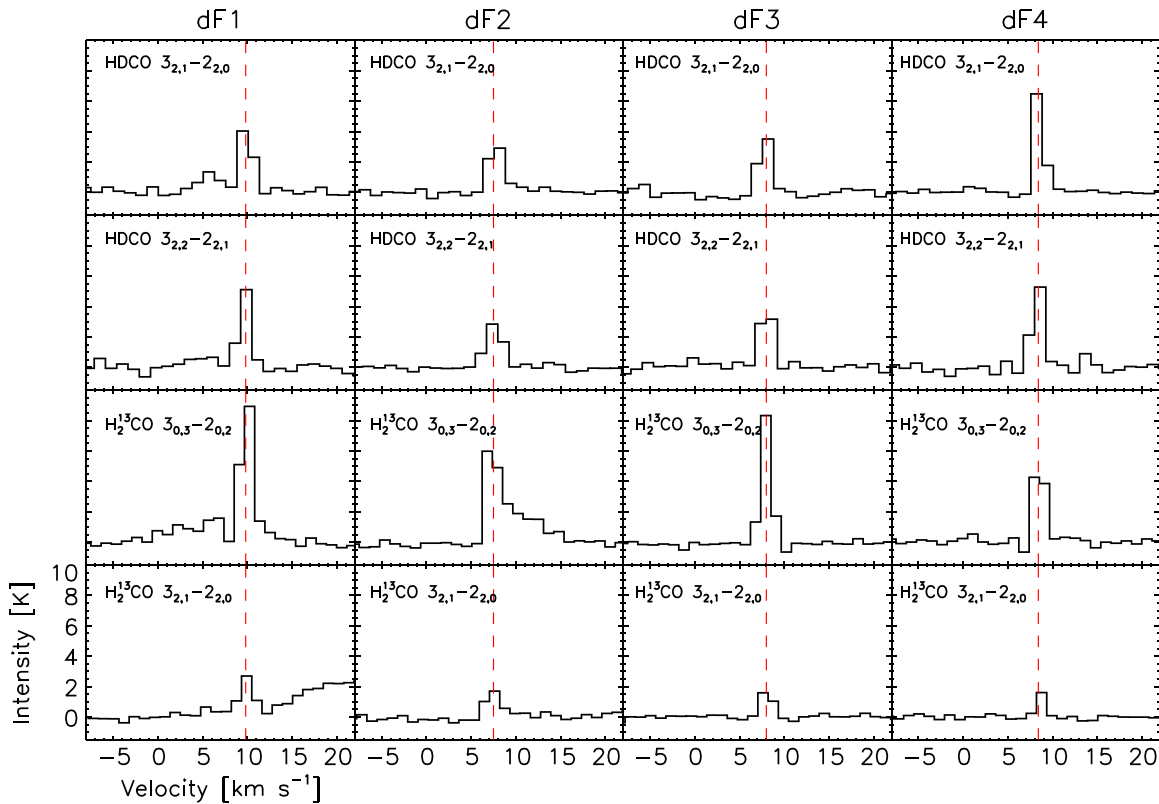


Figure 4. HDCO and H_2^{13}CO spectra observed toward dF1, dF2, dF3, and dF4. The red dashed line indicates the v_{LSR} toward each peak (i.e., 9.8, 7.5, 8.0, and 8.4 km s^{-1} , respectively).

SMA observations. A notable result is that the spatial distribution of formaldehyde emission (HDCO and H_2^{13}CO , see Figure 2) clearly differs from that of (deuterated) methanol (see Figure 3 of Peng et al. 2012). The methanol distribution follows a V-shaped structure linking the Hot Core component to the Compact Ridge (Peng et al. 2012) while formaldehyde exhibits a spatial structure which appears to surround this molecular V-shaped structure on four sides. This difference is illustrated in Figure 2 (bottom right panel) in which the deuterated methanol emission peaks identified by Peng et al. (2012) are indicated on the HDCO integrated emission map at 193391.6 MHz. Furthermore, the D/H ratio for methanol derived by Peng et al. (2012) lies in the range $(0.8\text{--}1.3) \times 10^{-3}$, which is up to an order of magnitude (within the uncertainties) lower than the D/H ratio for formaldehyde derived in this study (see Table 2).

4.2. Origin of Formaldehyde Emission

All the nearby well-characterized sources (i.e., Hot Core and Compact Ridge) are not coincident with formaldehyde emission. In fact, it is possible and even likely that we are seeing quiescent material surrounding the hotter sources, such as the well-known quiescent ridge in Orion-KL. Incidentally, the spatial difference between the formaldehyde and methanol emission has already been observed toward other sources, such as the Horsehead Photon-dominated Region (PDR) and its associated dense core (Guzmán et al. 2013) and the Orion Bar PDR (Leurini et al. 2006, 2010). In their respective analyses, the authors have shown that the UV radiation field affects the gas-phase abundance of formaldehyde and methanol. More specifically, the $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ abundance ratio is

expected to be higher in high-FUV illuminated environments compared with denser and less illuminated regions. In this light, the entire Orion-KL quiescent ridge gas is a face-on PDR (see Irvine et al. 1987; Persson et al. 2007; Lerate et al. 2008), and therefore the photodissociation of gas-phase methanol into formaldehyde might occur (e.g., see, Le Teuff et al. 2000; Leurini et al. 2006, 2010). In this context, we determine the abundance ratio of $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ in the formaldehyde clumps. Comparison to ratios measured toward other PDRs would then illuminate whether the Orion PDR is influencing the local chemistry of dense material surrounding the hot embedded cores.

The determination of the methanol column density (see Equation (2)) relies on the assumptions that the CH_3OH -E transitions listed in Table 3 are optically thin and that the rotational temperature is the same as that of H_2^{13}CO . It is important to note that toward the dF1 and dF2 emission peaks, the CH_3OH -E lines are strongly blended (see Figure 6), preventing us from deriving the column density of methanol at those positions. Regarding the dF3 and dF4 regions, the resulting $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ abundance ratio lies in the range 3.5–4.5, which might suggest a slight decrease in the methanol abundance in the quiescent ridge. However, our derived ratio is lower by at least a factor of 3–400 compared with that estimated by Leurini et al. (2010) toward the Orion Bar, suggesting that the production of formaldehyde in Orion-KL through the photodissociation of gas-phase methanol is not the main formation route. Finally, it is notable that our estimated $\text{H}_2\text{CO}/\text{CH}_3\text{OH}$ abundance ratio is more consistent with that found in hot-corino regions (see Maret et al. 2004, 2005 and Guzmán et al. 2013 for a review). This finding leads us to

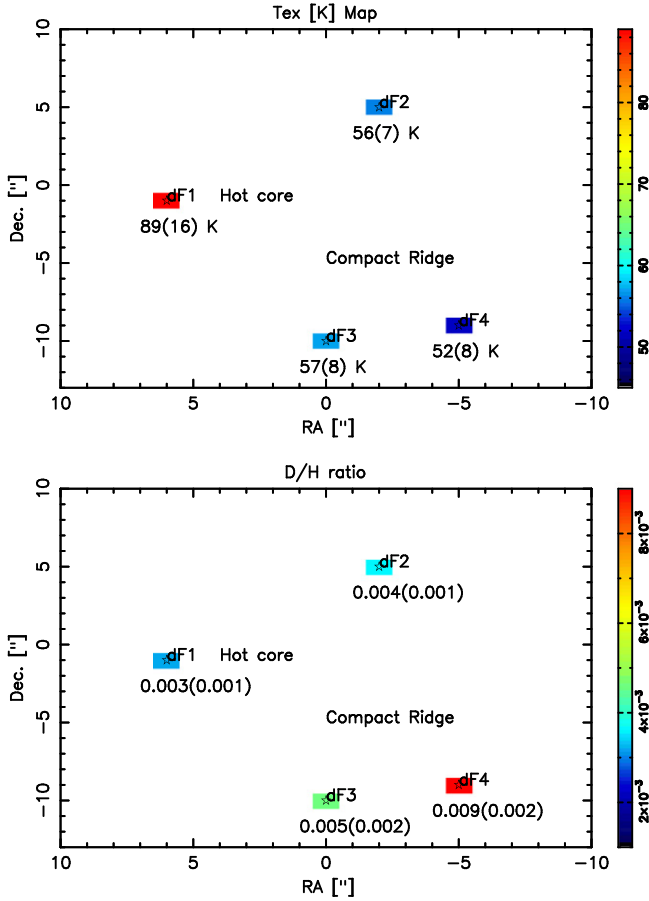


Figure 5. Top: H_2^{13}CO excitation temperature map toward Orion-KL. Bottom: D/H ratio for formaldehyde within Orion-KL.

argue that formaldehyde emission in Orion-KL is more likely probing the edge of the hot gas.

4.3. Implications: On the Formaldehyde Formation

Formaldehyde and methanol are believed to be formed on ice grain mantles during the pre-stellar cold phase ($T < 50$ K) from successive hydrogenation reactions of H or D atoms with CO (see, e.g., Charnley et al. 1997; Watanabe & Kouchi 2002; Cazaux et al. 2011; Taquet et al. 2012):



and



Table 2
Total Formaldehyde Column Densities and D/H Ratios

Position	$N(\text{HDCO})$ ($\times 10^{14} \text{ cm}^{-2}$)	$N(\text{H}_2^{13}\text{CO})$ ($\times 10^{14} \text{ cm}^{-2}$)	$N(\text{H}_2\text{CO})$ ($\times 10^{16} \text{ cm}^{-2}$)	D/H Ratio
dF1	4.81(0.62)	21.70(2.72)	15.20(1.90)	0.0032(0.0008)
dF2	2.86(0.20)	11.30(1.22)	7.92(0.86)	0.0036(0.0006)
dF3	2.94(0.67)	9.06(1.00)	6.34(0.70)	0.0046(0.0016)
dF4	3.99(0.54)	6.34(0.85)	4.44(0.60)	0.0090(0.0024)

Note. The total H_2^{13}CO and H_2CO column densities have been derived assuming an ortho:para ratio of 3:1 (e.g., see Kahane et al. 1984; Crockett et al. 2014) and a $^{12}\text{C}/^{13}\text{C}$ isotopic ratio of 70 (e.g., see, Favre et al. 2014).

Table 3

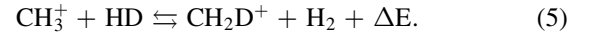
Spectroscopic Parameters of the CH_3OH -E Methanol Transitions Observed with the SMA Towards the dF3 and dF4 Emission Peaks^a

Frequency (MHz)	Transition	E_{up} (K)	A ($\times 10^{-5} \text{ s}^{-1}$)
193415.37	$4_{0,4}-3_{0,3}v_t = 0$	36.3	3.03
193441.61	$4_{1,4}-3_{1,3}v_t = 0$	28.8	2.84
193474.33	$4_{3,1}-3_{3,0}v_t = 0$	70.9	1.33
193488.99	$4_{3,2}-3_{3,1}v_t = 0$	85.9	1.33
193506.60	$4_{1,3}-3_{1,2}v_t = 0$	44.3	2.91

Note.

^a Measured and predicted transitions are available from the CDMS database (Müller et al. 2005) and at Splatalogue (www.splatalogue.net, Remijan et al. 2007).

Laboratory experiments have shown that the sequential CO hydrogenation process (i.e., Reaction (3)) efficiently forms both formaldehyde and methanol at low temperatures (≤ 20 K, see Hidaka et al. 2004; Watanabe et al. 2004; Fuchs et al. 2009). Thus, if methanol and formaldehyde both purely originate from ice grain mantles, the measured D/H ratio should be similar (within a factor of two) for both molecules, and, in particular, these molecules should trace similar environments while desorbed as they share a common origin. This is inconsistent with our observations (see Section 4.1), and thus strongly argues in favor of differences in the chemical formation pathways of these deuterated molecules. Thus, CH_3OH and H_2CO emission is probing different spatial regions within the central region of Orion-KL that may not be coeval. We infer that a likely scenario is HDCO production through hot gas-phase deuterium chemistry in the colder gas associated with Orion-KL, as suggested by Loren & Wootten (1985). More specifically, at relatively high temperatures ($T \sim 70$ – 100 K, Wootten 1987; Öberg et al. 2012), such as that derived in this study (see Figure 5), reaction (5) is active due to its high exothermicity (ΔE of 654 K, see Roueff et al. 2013) and favors deuterium fractionation through reactions involving CH_2D^+ as a parent molecule (Favre et al. 2015):



In that context, reaction (5) can then lead to the formation of HDCO and H_2CO (see further details in Loren & Wootten 1985). Incidentally, the temperature of this colder region associated with Orion-KL is not sufficient to desorb CH_3OH from the surface of icy grain mantles ($T \geq 120$ – 160 K; see

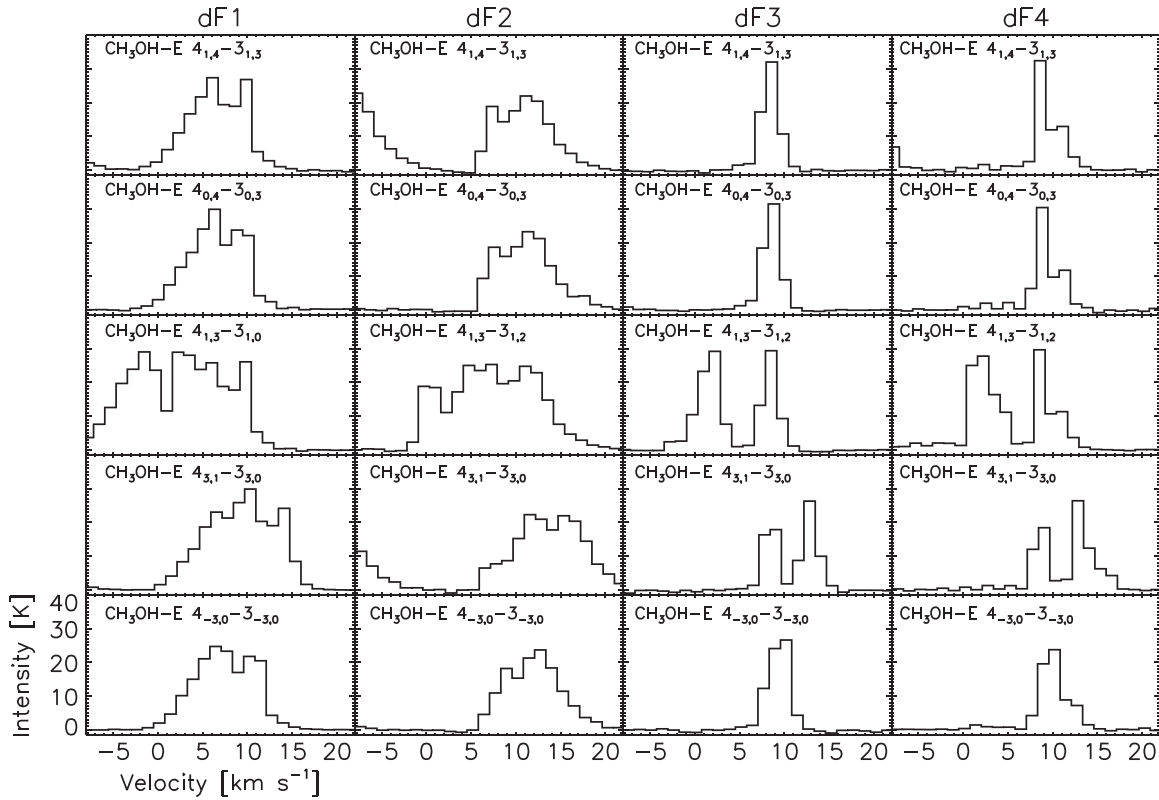


Figure 6. CH₃OH-E spectra observed toward dF1, dF2, dF3, and dF4.

Collings et al. 2004; Green et al. 2009). However, in the inner hottest part of Orion-KL where methanol emits, most of the formaldehyde might have been converted into methanol by grain-surface reactions (Watanabe & Kouchi 2002) during a colder phase prior to the explosive event. Then, upon heating, methanol is released from grain surfaces into the gas phase along with little formaldehyde. We stress that the release of methanol into gas phase in this region is mainly due to internal radiation heating (i.e., outflow, shock, IR sources) but not heat from the PDR (see Section 4.2). In this instance, the D/H ratio and the spatial distribution of methanol should differ from that of formaldehyde.

5. CONCLUSIONS

We have characterized, for the first time, the spatial distribution of deuterated formaldehyde (HDCO) toward Orion-KL with an angular resolution of $3''.4 \times 3''.0$ using the SMA. The new SMA broadband capability of the 230 GHz band allowed simultaneous observation of both HDCO and H₂¹³CO within relatively sparse spectra. Four main emission peaks, labeled in this study dF1 to dF4, are identified in the formaldehyde emission image. An important result is that the spatial distribution the emission of the HDCO and H₂¹³CO emission differ from that of CH₃OH and its deuterated isotopologues. The emission maps show that methanol emits in the inner part of Orion-KL, while formaldehyde is found in the colder gas enveloping the CH₃OH emission on four sides: one located left of the Hot Core (dF1), one toward the north of the Compact Ridge (dF2), and two in the quiescent ridge (dF3 and dF4). In addition, we derive a HDCO/H₂CO ratio which lies in the range 0.003–0.009 within the region; this value is an

order of magnitude higher than the D/H measured for methanol. We suggest that the high measured D/H ratio for formaldehyde and its spatial distribution in Orion-KL are a combination of gas-phase chemistry in the cooler gas associated with Orion-KL, and a conversion of formaldehyde into methanol on ice grain mantles in the earlier history of the inner part.

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Facility: SMA.

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